

## **BROADSCREEN GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) METHODS**

### **Sample Concentration**

All water samples (39 L) were concentrated by adsorption on resins (Amberlite XAD, Supelco). Details about the preparation and cleaning of these resins can be found elsewhere (Richardson et al., 1994). Water samples were acidified to pH 2 by the addition of hydrochloric acid prior to passage through the columns containing a combination of resins (XAD-8 over XAD-2). A maximum ratio of 770:1 (v/v) of water to resin was used to maximize the adsorption of organic compounds and to minimize breakthrough. The columns were eluted with ethyl acetate, and residual water was removed from the ethyl acetate eluents by using separatory funnels to drain off the water layers, followed by the addition of sodium sulfate. Samples were further concentrated by rotary evaporation (to approximately 5 mL), followed by evaporation with a gentle stream of nitrogen (to a final volume of 1 mL).

Raw, untreated water was collected at each sampling to enable the distinction of chemicals that were formed as disinfection by-products (DBPs) in the treatment process from chemical pollutants that were already present in the raw water. In addition to the raw water controls, four blanks were also analyzed: (1) ethyl acetate passed through the XAD resins and concentrated in the same manner as the treated samples; (b) deionized, distilled water passed through the XAD resins and concentrated; (c) deionized, distilled water treated with chlorine and concentrated; and (d) deionized, distilled water treated with chloramine and concentrated. The latter two blanks were done to determine whether there were any artifacts due to reaction of secondary disinfectants with the ethyl acetate or with resin impurities. As compared to the raw water samples and the treated samples, these blanks contained relatively few compounds.

### **Derivatizations**

Methylation derivatizations with boron trifluoride in methanol were used to aid in identifying carboxylic acids (Kanniganti et al., 1992), and pentafluorobenzylhydroxylamine (PFBHA) derivatizations were used to identify polar aldehydes and ketones (Sclimenti et al., 1990).

### **GC/MS Analysis**

High-resolution GC/electron ionization (EI)-MS and GC/chemical ionization (CI)-MS analyses were performed on a hybrid high-resolution mass spectrometer (VG 70-SEQ, Micromass, Inc.) equipped with a GC (Model 5890A, Hewlett-Packard-Agilent). The high-resolution mass spectrometer was operated at an accelerating voltage of 8 kV. Low-resolution analyses were carried out at 1000 resolution and high-resolution analyses at 10,000 resolution. Positive CI experiments were accomplished by using methane gas. Injections of 1–2  $\mu$ L of the extract were introduced via a split/splitless

injector onto a GC column (DB-5, 30-m  $\times$  0.25-mm ID, 0.25- $\mu$ m film thickness, J&W Scientific-Agilent). The GC temperature program consisted of an initial temperature of 35°C, which was held for 4 min, followed by an increase at a rate of 9°C/min to 285°C, which was held for 30 min. Transfer lines were held at 280°C, and the injection port was controlled at 250°C. Duplicate analyses were also carried out with the GC injection port held at 140°C to enable the analysis of trihalonitromethanes (THNMs). In previous work, THNMs were found to decompose at temperatures higher than 170°C (Chen et al., 2002).

## Chemical Standards

The following chemicals were prepared synthetically and provided by Can Syn Chem. Corp. (Toronto, ON, Canada): dichloriodomethane, bromochloriodomethane, iododibromomethane, diiodochloromethane, diiodobromomethane, 2,2-dibromopropanoic acid, 3,3-dibromopropenoic acid, cis-2,3-dibromopropenoic acid, tribromopropenoic acid, 2-bromobutanoic acid, cis-2-bromo-3-methylbutenedioic acid, trans-2,3-dibromobutenedioic acid, bromonitromethane, dichloronitromethane, bromochloronitromethane, bromodichloronitromethane, 1,1-dibromopropanone, 1,1,1-tribromopropanone, 1,1-dibromo-3,3-dichloropropanone, 1,3-dibromo-1,3-dichloropropanone, and 1,1,3-tribromo-3-chloropropanone. 1,1,3,3-Tetrabromopropanone and dibromonitromethane were prepared synthetically and provided by Majestic Research (Athens, GA). These chemicals were used to confirm tentative identifications made by mass spectrometry. All other chemicals used for broadscreen analyses were purchased at the highest level of purity from Aldrich, Chem Service, and TCI America.

## Identification of DBPs

For qualitative identification work, the criteria used for listing an identified compound as a DBP was its presence in the treated-water samples in quantities at least 2–3 times greater than in the untreated, raw water (as judged by comparing GC peak areas). It was important to distinguish a compound as a DBP, even if small amounts of the compound were present in the raw water, because many compounds that are common pollutants (or natural contaminants in water) have also been proven to be DBPs.

GC/MS chromatograms were carefully analyzed for the presence of chemicals that were produced in the treated samples. Each mass spectrum was carefully background-subtracted to remove closely eluting or co-eluting peaks, after which the NIST, Wiley, and Athens-EPA mass spectral library databases were searched for a match of the unknown's mass spectrum. Several common DBPs, such as haloacetic acid methyl esters, could be quickly identified through a library database match using the large NIST (>100,000 spectra) and Wiley databases (>200,000 spectra). In addition, the user library database created at the USEPA laboratory in Athens, GA (>200 spectra, mostly DBPs) also enabled a rapid identification of many less common DBPs, such as 1,1,3,3-tetrabromopropanone and bromochloriodomethane. Even with a definitive library match, however, these identifications are listed as tentative until a match of the unknown's GC retention time could be made with an authentic chemical standard. Only

when both the mass spectrum and the retention time matched were the DBPs listed as 'confirmed'.

Despite the large size of the library databases and the user library that had been created at the USEPA-Athens, there were many new DBPs identified in this study that required significant interpretation to enable their identification. This process involved an initial study and interpretation of the low resolution GC mass spectrum. Ion fragments and losses from the molecular ion were studied to postulate a tentative structure. The presence or absence of the molecular ion was determined, and CI-MS was used when the molecular ion was not present or to confirm a molecular ion that was present. Next, high resolution EI-MS analyses were made, which allowed the mass-to-charge ( $m/z$ ) ratio of an ion to be determined to 3 decimal places. For example, by low resolution mass spectrometry, a molecular ion can only be assigned a nominal mass (e.g.,  $m/z$  200). With high resolution mass spectrometry, this ion can be measured with greater accuracy (e.g.,  $m/z$  200.012). With this exact mass, generally a single empirical formula (number of carbons, hydrogens, oxygens, nitrogens, etc.) can be assigned to the ion. High resolution EI-MS was used not only for the molecular ions, but also for the fragment ions, which generally reduced the number of possible empirical assignments from 6-8 to one.

Once the empirical formulas were known, functional groups could be postulated and overall structures assigned. All possible isomers were considered when making these tentative assignments. When it was not possible to choose a particular isomer as the correct assignment for the unknown DBP, an attempt was made to purchase or obtain a synthetically produced, authentic chemical standards of all the possible isomers so that a definitive match could be made (of both mass spectra and retention time). When the identification of a compound was confirmed through the analysis of an authentic chemical standard, it was denoted in italics in this report. All other DBP identifications should be considered tentative.

## REFERENCES

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